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GEO. T. WINSTON, LL.D., DIRECTOR



# The Relative Values of Some Nitrogenous Fertilizers

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WEST RALEIGH, N. C



Publications sent to any address in North Carolina on application.

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# The Relative Values of Some Nitrogenous Fertilizers.

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The value of any fertilizer depends on its availability to the plant—that is, the readiness with which it can be absorbed directly by the plant, or converted into forms which can be assimilated. Nitrogen can be assimilated by plants directly in four forms, viz.: (1) free nitrogen, (2) as certain organic compounds, (3) as ammonium salts, (4) as nitrates.

Free nitrogen can be assimilated from the air by a class of plants with the aid of organisms living in nodules on their roots. This method of assimilation is confined to the Leguminosæ, which include clover, peas, beans, the peanut, vetch, etc.

Some organic compounds, such as urea, glycocoll, leucin, tyrosin asparagin, and acetamide, may be taken up directly by plants, and serve to nourish them. All of these compounds may occur in the soil. Urea is found in urine, asparagin in plants, and asparagin and tyrosin are often produced by the decay of animal or vegetable matter in the soil. All organic compounds applied to the soil change to nitrates with greater or less rapidity, and in this form are readily taken up by the plant.

Ammonium salts also can be assimilated by plants. German millet, golden millet, watermelons, corn, common sorrel, and other plants, seem to be able to assimilate ammonium salts directly. Ammonium salts also are converted to nitrates when placed in the soil.

While some plants can assimilate free nitrogen, others organic compounds, and others nitrogen in the form of ammonia, nitrates appear to be the form in which nitrogen is taken up with the greatest readiness by most plants. It is also the form which all nitrogen compounds finally assume when placed in the soil.

Different classes of plants behave differently towards these different forms of combination of nitrogen. Some prefer one form, some another, and it is probable that many plants assimilate their nitrogen in several forms. The same plant may act differently at different stages of growth. Some are not benefitted by ammonium salts when young, and others are; some feed on nitrates during the entire period of their growth, and others are not benefitted by them until they have attained some size.

When combined nitrogen, in whatever form of combination, is placed in the soil, it is converted into ammonium salts, nitrites and finally nitrates, with greater or less speed, depending on the form of combination, the temperature, condition of the soil, etc., provided certain living organisms are present (and they usually are). If in any given soil, we determine the relative rate with which nitrogenous fertilizers which can not be utilized directly by the plant, are converted into nitrates, it should throw some light upon the relative values to plants of those particular fertilizers.

This is the object of the work which will be described in the following pages.

HISTORICAL.

Muntz and Girard [Central Blatt f. agr. Chem., 20, 656 (1891), abs.] have determined the relative rate of nitrification of some fertilizers. A small quantity of the fertilizer was intimately mixed with natural soil, and kept at the temperature of 15-25 degrees C, properly moistened, and at the end of a given period leached with water, and the nitrate determined in the extract. The nitrate existing in the soil at the beginning of the experiment was previously determined. The time was 30, 32 and 39 days for different sets. The nitrogen converted into nitrates, and the nitrogen recovered from the soil by horse-tooth corn in two years, is shown in the following table:

| | Nitrified in 30 Days. | Recovered by Corn. |
|---|---|---|
| | *Per Cent.* | *Per Cent.* |
| Ammonium sulphate | 75.0 | 76.7 |
| Dried blood | 72.4 | 55.0 |
| Roasted horn, fine | 71.0 | 60.1 |
| Flesh meal | 70.4 | ........... |
| Horn Trimming, fine | 55.5 | 53.3 |
| Poudrette, rather coarse | 18.1 | 14.9 |
| Roasted Leather, fine | 11.6 | 38.3 |
| Leather chips, raw | 0.4 | ........... |

In another series, the order of nitrification was as follows: Bat guano, dried grasshoppers, dried cockchafers, flesh meal, dried blood, (the substance nitrified to the greatest extent being given first). There is very little difference between the three substances named last. The nature of the soil has a great influence on the change. Nitrification was most active in a light soil from Joinville (used in the experiment referred to above), then in a garden soil, then in a chalky soil, then in a marled moor soil. Very little nitrification occurred in a very calcerous clay, except with cow manure, and yellow lupines, which loosened their texture, and none in an acid moor soil, with the same two exceptions.

P. Boname (Exp. Sta. Record, 9, 732 abs.) determined the nitrates in the drainage water from a sandy soil deficient in lime to which fertilizers had been added. The order of nitrification at the end of the first month was found to be, fish guano (most rapid), blood, fertilizer, oil cake, and ammonium sulphate. When calcium carbonate was added, nitrification took place more rapidly, but the order was still dried blood, oil cake, ammonium sulphate. (See Table I.)

TABLE I.

Nitrate nitrogen in 100 grams soil (in mgr.)

| | 1 Month. | 2 Months. | 3 Months. |
|---|---|---|---|
| Soil | 4.2 | 5.0 | 5.0 |
| Soil and ammonium sulphate | 22 | 29 | 35 |
| Soil and dried blood | 66 | 74 | 85 |
| Soil and oil cake | 59 | 82 | 95 |
| Soil and fish guano | 74 | 110 | 113 |
| Soil and calcium carbonate | 6.2 | 7.3 | 6.0 |
| Soil, calcium carbonate, and ammonium sulphate | 75 | 133 | 186 |
| Soil, calcium carbonate, and dried blood | 123 | 151 | 159 |
| Soil, calcium carbonate, and oil cake | 97 | 139 | 137 |

It will be noted that where calcium carbonate was not used, nitrates were formed more slowly through the entire period from ammonium sulphate than from the organic substances used. When calcium carbonate was added, the quantity of nitrates produced for the first and second months from ammonium sulphate was smaller than from the organic substances. At the end of the third month, a larger quantity of nitrates was formed from ammonium sulphate than from the organic materials.

EXPERIMENTAL—EFFECT OF DILUTION OF SOIL.

The effect of ratio of soil to fertilizer was studied in some preliminary experiments. Three thousand grammes of a sandy soil from a pasture, which had been sifted through a six-mesh sieve, was mixed well with the quantity of dried blood, containing 1.0, 0.5, 0.25 gram. nitrogen, and the mixtures placed in a dark closet for fourteen days. They were watered at suitable intervals, endeavoring to maintain the original 10 per cent of water. The temperature was about 27 degrees C. The nitrates were leached out at the end of the period, and their quantity determined by the Tiemann-Schulze method. Results in Table II.

TABLE II.

| | Dilution. | Gram. Nitrates. | Nitrified. |
|---|---|---|---|
| | | | *Per Cent.* |
| Soil | | 0.0963 | |
| Soil and 1.0 gram N | $\frac{1}{3000}$ | 0.4564 | 36.0 |
| Soil and 0.5 gram N | $\frac{1}{6000}$ | 0.3626 | 52.3 |
| Ditto and 1.785 gram calcium carbonate | | 0.5043 | 81.6 |
| Soil and 0.25 gram N | $\frac{1}{12000}$ | 0.2354 | 55.6 |

The rapidity of the nitrification is influenced very decidedly by the dilution, and increased by calcium carbonate from 100 to 156. Thirty pounds of nitrogen per acre is a liberal application for a fertilizer. Assuming that the mean weight of a cubic foot of soil is eighty pounds, and that the soil is cultivated to the depth of six inches, then the dilution of the nitrogen applied as a fertilizer is 1-57000, which is much greater than in any of the above cases. But it must be remembered that a fertilizer is never mixed intimately with the soil, and is often in lumps, so that the actual soil surface in contact with the fertilizer is probably much less than 1-12000. This would be particularly true with materials like dried blood, which are insoluble in water. Soluble fertilizers, like ammonium sulphate, would diffuse until they become fixed, or the soil water becomes of a uniform composition; the diffusion of salts in a soil must be a very slow process.

### RATE OF NITRIFICATION.

The experiments to determine the relative rate of nitrification were carried out as follows: The fertilizing materials were those sent out by the referee of the Association of Official Agricultural Chemists for 1900, to test the methods for determining the availability of nitrogen. A sandy clay soil from a pasture was sifted through a coarse sieve (six meshes to the inch), and a quantity of material equivalent to 0.6 gramme nitrogen was intimately mixed with 1,000 gram. of the soil. The soil was then placed in precipitating jars, and kept in a dark closet, enough water being added to raise the percentage from 6.3 to 11.6 per cent. At suitable periods, three of the jars were weighed, and the estimated loss of water was replaced in all the jars. The temperature was 28-30 degrees C, and the time was three weeks. When calcium carbonate was added, the amount was exactly sufficient to combine with the nitrogen of the fertilizer if the entire amount were converted to nitric acid. At the end of the experiment, the nitrates were leached out, and the amount determined by the Tiemann-Schulze method. The amount of nitrates found in a blank experiment was deducted from the total. The results are given in Table III.

On account of the surprisingly small percentage of ammonium sulphate nitrified in the first series, the experiments with cotton-seed meal and ammonium sulphate were repeated, the time being 26 days, the temperature 23-26 degrees C, and the sample being moistened as before. The soil was taken from the same pasture as in the first series, but differed from it somewhat, as is shown by the fact that it contained 0.1641 gram. nitrogen as nitric acid per kilogramme, whereas the former contained only 0.0595 gram.

RATE OF NITRIFICATION AND AVAILABILITY OF NITROGEN.

We have selected, and give below (Table III.), the results obtained by vegetation tests with oats and Hungarian grass by Jenkins and Britton (Conn. State Station Report 1897, 357) and those obtained by Bizzell in the laboratory of this Station with the pepsin-hydrochloric acid method, and the neutral permanganate method, the materials being those used in these nitrification experiments.

TABLE III.

| | RATE OF NITRIFICATION. | | | | AVAILABILITY. | | |
|---|---|---|---|---|---|---|---|
| | Without— | | With $CaCO_3$ | | Soluble $KMnO_4$ | Pepsin HCl | Veg. Test. |
| | Per Ct. | Rank | Per Ct. | Rank | | | |
| *Series I.* | | | | | | | |
| Dried blood | 34.8 | 100 | 54.9 | 100 | 94.4 | 94.7 | 73.3 |
| Cottonseed meal | 33.9 | 97 | 54.8 | 100 | 91.1 | 91.1 | 64.8 |
| Dried fish | 30.3 | 87 | 46.5 | 85 | 88.7 | 67.3 | 63.9 |
| Tankage | 26.2 | 75 | 34.8 | 63 | 88.3 | 56.4 | 49.4 |
| Bat guano | 22.4 | 64 | 35.8 | 65 | 75.1 | 56.4 | --- |
| Bone | 18.9 | 54 | 16.6 | 30 | 64.2 | 92.3 | 16.7 |
| Bone (six weeks) | 21.7 | ------ | 17.4 | ------ | ------ | --- | --- |
| Ammonium sulphate | 1.3 | 4 | 31.1 | 55 | 100 | 100 | ------- |
| Nitrate of soda | ---- | ------ | ---- | ----- | 100 | 100 | 100 |
| *Series II.* | | | | | | | |
| Cottonseed meal | 26.7 | ------ | ---- | ------ | ------ | ------- | ------ |
| Ammonium sulphate | 3.4 | ------ | 32.6 | ------ | ---- | ------- | |

The order of availability as determined by the neutral permanganate method, and by the vegetation experiments, is the order of nitrification, except in the case of ammonium sulphate. The pepsin-hydrochloric acid method places bone next to blood, and above cottonseed meal, where it does not belong.

The mechanical condition of the material would, of course, have great effect on the rate of nitrification. It is quite possible that the organic fertilizers contain two or more nitrogen compounds of different degrees of susceptibility to the nitrifying organisms. Bone was nitrified to the extent of 18.9 per cent in three weeks, and only 21.7 per cent in six weeks.

## EFFECT OF CALCIUM CARBONATE.

Taking the quantity of nitrates formed without the presence of calcium carbonate as 100, the quantity formed with it present was, with dried blood, 158; cottonseed meal, 162; dried fish, 153; tankage, 133; bat guano, 160; bone (three weeks), 88; bone (six weeks), 80; ammonium sulphate, 2390; ammonium sulphate (Series II.), 959. This effect may depend on the quantity of bases present in the material. The rate of nitrification of bone, which contains large quantities of calcium salts, is actually decreased by the addition of calcium carbonate while that of ammonium sulphate is increased enormously. These results show the beneficial influence of lime in rendering nitrogenous fertilizers available, and explain in part why lime is so beneficial to many crops. When ammonium sulphate is used as a fertilizer, it would be advisable to add calcium carbonate at the same time, in many cases.

## NITRIFICATION OF AMMONIUM SULPHATE.

As regards ammonium sulphate, in a soil deficient in lime, it is nitrified less readily than any other of the fertilizing materials tested. In the soil to which calcium carbonate had been added, the rate of its nitrification still falls below that of cottonseed meal, blood, and dried fish, and was in one series less, the other greater, than tankage and bat guano, but the average was below. In Boname's experiments ammonium sulphate was nitrified during the first and second months less rapidly than any of the other fertilizing materials used (blood, oil cake, guano,) whether calcium carbonate was added or not. On the contrary the experiments of Muntz and Girard (presumably in a soil containing calcium carbonate) place ammonium sulphate at the head of all the fertilizing materials tested (blood, flesh meal, poudrette, roasted leather, leather chips).

There are three possible ways to account for the slow rate of nitrification of ammonium sulphate.

1. Ammonium sulphate may hinder the action of the nitrifying organisms. The soil in question contained 2.5 gram. ammonium sulphate dissolved in 100 gram. soil water. It is known that various salts will retard the nitrifying activity of the organisms if present in too large quantity. Deherain found that common salt began to be harmful when more than 0.1 per cent of the weight of the soil was added, and with larger quantities nitrification almost ceased. Large additions of nitrate of soda also decrease the rate of nitrification.

This explanation will not account for the beneficial action of calcium carbonate, for if double decomposition takes place, the ammonium carbonate formed is more of a hindrance to the germs than the ammonium sulphate.

The assumption that ammonium sulphate hinders the action of the nitrifying organism would explain the low rate of nitrification of ammonium sulphate that we have obtained. It would also explain the results of Boname (already cited), according to which ammonium sulphate is nitrified very slowly indeed the first and second months, and very rapidly the third. In direct contradiction to the above hypothesis, however, would stand the experiments of Muntz and Girard, who found that, in thirty days, ammonium sulphate was nitrified to a greater extent than dried blood, etc., and those of Th. Schloesing [Central Blatt f. agr., Chem., 19, 1 (1890), abs.] The latter found, that at the end of 56 days, ammonium chloride added to a soil at the rate of 3.58 gram. per kilo. (1.8 gram. per 100 cc. of soil water), was almost completely nitrified, and the same occurred with ammonium sulphate at the rate of 2.7 gram. per kilo. (1.4 gram. per 100 cc. soil water) in 22 days, and ammonium carbonate at the rate of 0.53 gram. ammonia per kilo., in 28 days. The soil contained 19.4 per cent water.

These difficulties might be explained away by supposing that the ammonium sulphate affects the nitrifying germs less in some soils than in others, either on account of the different character of the soils (power of fixing ammonia, etc.), or the presence of different kinds of nitrifying organisms.

If the ammonium sulphate is detrimental to the nitrifying organisms, the same kind of action would take place when it is used as a fertilizer, though perhaps to a less degree. Each lump of the salt would become a center from which would diffuse a solution of ammonium sulphate, detrimental to the nitrifying organisms. The time required for this unfavorable condition to disappear, would depend on the rate of diffusion of the salt, soil moisture, rain-fall, etc.

2. The second explanation for the slow rate of nitrification of ammonium sulphate, compared with the other materials, is that the nitric and sulphuric acids formed are detrimental to the nitrifying organisms, being neutralized only in part by the bases of the soil. When calcium carbonate is added, it neutralizes the acids, with consequent acceleration of the change. This explanation is probably applicable, but does not explain all the facts, for, if so, the addition of calcium carbonate would remove the unfavorable conditions, and place ammonium sulphate at the head of the list—which it does not do.

3. The third explanation is, that different soils contain different nitrifying organisms, some of which convert organic matter directly to nitrites, while others change ammonium salts to nitrites more readily. The nitrites are then converted to nitrates. In soils containing the first kind of organisms, and few of the second, organic

matter would be converted to nitrites more rapidly than ammonium salts would be, as was the case in the experiments of Boname, and those here described. In soils in which the second class of organisms predominate, ammonium salts would be nitrified more rapidly than organic compounds. This hypothesis would explain all the experiments here cited.

It appears very probable that all three of the explanations given above apply, and that all three are in operation, one exerting a greater influence in some soils than others. It is the purpose of this Station to continue the experiments on nitrification, with a view to test all the problems that may arise.

## CONCLUSIONS.

1. The nitrification of blood takes place more rapidly when it is mixed with a large quantity of soil than with a small quantity.

2. The order of nitrification in the soil used was, dried blood (most nitrified), dried fish, tankage, bat guano, bone, ammonium sulphate. Excluding the ammonium sulphate, this is the order of availability, as measured by vegetation tests, and solubility in permanganate of potash.

3. When calcium carbonate was added to the soil, the nitrification was greatly accelerated, and the order became dried blood, cottonseed meal, dried fish, bat guano, tankage, ammonium sulphate, bone.

4. When ammonium sulphate is used as a fertilizer, in most cases it would be advisable to add calcium carbonate in some form also.

5. The low rate of nitrification of ammonium sulphate is probably due to the presence of organisms which nitrify organic compounds in preference to ammonium salts. The presence of the ammonium sulphate may also hinder the activity of the nitrifying organisms. The acids formed may also be a hindrance when no base is present to neutralize them. All three of these causes may be in operation at the same time.